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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/NL87/00010 (22) International Filing Date: 12 May 1987 (12.05.87) (31) Priority Application Number: 8601225 (32) Priority Date: 14 May 1986 (14.05.86) (33) Priority Country: NL (71) Applicant (for all designated States except US): RIJKSUNIVERSITEIT TE UTRECHT [NL/NL]; Heidelberglaan 8, NL-3584 CS Utrecht (NL). (72) Inventor; and (75) Inventor/Applicant (for US only) : DUR, Ignatius, Cornelius, Johannes [NL/NL]; Padualaan 8, NL-3584 CH Utrecht (NL). (74) Agents: VAN DER BEEK, George, Frans et al.; Nederlands Octrooibureau, Johan de Witlaan 15, P.O. Box 29720, NL-2502 LS The Hague (NL).		(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i>
(54) Title: METHOD FOR THE APPLICATION OF A POLYTETRAFLUOROETHYLENE COATING TO GLASS (57) Abstract <p>Method for the application of a polytetrafluorethylene (PTFE) coating to glass i.e. to both flat glass and glass objects such as dishes and the like; said method is characterized in that (a) the glass is subjected to a blasting treatment with an abrasive containing SiO₂ preferably quartz glass; (b) the blasted surface of the glass is treated with an etchant like HF; (c) the treated surface of the glass is exposed to the action of a grease/oil-removing agent such as HNO₃ or H₂SO₄; (d) the glass with the oil/grease-free surface is dried with an organic drying agent like methanol and acetone; (e) the glass is then freed from the drying agent in a dry, clean atmosphere; and (f) PTFE is applied to the treated surface of the glass.</p>		

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Method for the application of a polytetrafluoroethylene coating to glass

The invention relates to a method for the application of a polytetrafluoroethylene (PTFE) coating to glass, both flat glass and glass objects such as dishes and the like being included under the term "glass".

As is known, it has already been possible for a considerable time to apply a PTFE coating to metal objects, in, inter alia, the household field, for example frying pans and saucepans, and also baking tins, which coating has the great advantage that the cleaning of such objects can take place in a simple and rapid manner after use.

An attempt has therefore been made to provide such an inert PTFE coating on glass objects in addition to the metal objects. However, despite intensive research, this has hitherto not been successful. The reasons for this very probably lie in the fact that the surface of glass which can be described as fairly inert, is completely different from that of metal objects. The problem which occurred in coating glass in particular, was that the PTFE exhibited no, or no satisfactory, adhesion to the glass and consequently easily came off the glass.

Surprisingly, the Applicant has now found a method for applying PTFE to glass which has been subjected to a special preliminary treatment.

The method according to the invention described in the introduction is characterized in that

- a) the glass to be coated is subjected to a blasting treatment with an abrasive containing SiO_2 ;
- b) the blasted surface of the glass is treated with an etchant;
- c) the treated surface of the glass is exposed to the action of a strong grease-/oil-removing agent;

- d) the glass with the oil-/grease-free surface is dried with an organic drying agent;
e) the glass is then freed from the drying agent in a dry, clean atmosphere; and
5 f) PTFE is applied to the treated surface of the glass.

More in particular the following may be stated in relation to the separate steps.

Step (a) of the method according to the invention is performed to increase and to roughen the surface
10 of the glass. However, in order not to damage the glass surface too much, an abrasive containing SiO_2 is used, the glass receiving a slightly matt surface. In this connection attention is drawn to the fact that if aluminium oxide (Al_2O_3) is used for blasting, the surface of
15 the glass becomes completely matt and the strength of the glass decreases considerably because of the great damage produced at the surface. Such an abrasive can therefore not be used in the method according to the invention.

In view of the above, it is emphasized that when
20 an abrasive containing SiO_2 , which advantageously contains as high a SiO_2 content as possible, for example at least 95% SiO_2 , is used for blasting, the strength of the glass remains ideal. Preferably, quartz glass with a particle size of 70-110 μm is used as abrasive.

25 In step (b) of the method according to the invention the blasted surface of the glass is treated with an etchant in order to clean the glass surface, i.e. to detach loose particles consisting of impurities from the glass surface and to make the roughening produced by the blasting more even. Advantageously, an HF solution in water,
30 preferably in a concentration of 5-15%, or a concentrated lye such as NaOH or KOH may be used as etchant.

In the third step, (c), of the method according to the invention the etched surface of the glass is treated
35 with a grease-/oil-removing agent, advantageously with concentrated acid such as HNO_3 or H_2SO_4 or concentrated hydrochloric acid. This concentrated acid removes in particular the last remnants of grease and oil which

are still present on the surface.

A further advantage of using concentrated acids of this type is the replacement of iron ions present in the glass surface by hydrogen ions from the concentrated acid. Said removal of the iron ions from the glass surface is considered useful in view of the fact that the presence thereof is apparently not conducive to the adhesion of the PTFE coating to the glass surface.

In step (d) the glass with the oil-/grease-free surface is dried with an organic drying agent. An alcohol such as methanol or ethanol or also other organic drying agents such as, advantageously, acetone may be used as the organic drying agent. The viscosity of the drying agent should be low in order that such a drying agent can easily penetrate into the pores of the glass surface and can entrain the residual quantity of water present therein.

In step (e) the glass is freed from the drying agent in a dry, clean atmosphere. Advantageously, clean air is used for this purpose and preferably purified compressed air. The use of normal compressed air is not advisable in view of the fact that in that case the risk is too great that dirt and oil particles of all types end up on the cleaned glass surface, which is not conducive to the adhesion of the PTFE coating to the glass surface.

The products marketed by E.I. du Pont de Nemours & Company under the tradename of "Teflon" may be used as PTFE products.

The invention is explained in more detail on the basis of the examples below. For this purpose Pyrex glass has been used in Examples I-IV and Symax glass in Example V, which types of glass were subjected to the following pretreatment:

- 1) Blasting with "industrial" quartz glass with a particle size of 70-110 μm ;
- 2) Rinsing with a 10% HF solution in water for 1 minute;
- 3) Rinsing with boiling nitric acid for 0.5 minute ;
- 4) Rinsing with methanol for 0.5 minute , and

5) Drying in the air or with well-filtered compressed air.

After the steps 1, 2 and 3 the glass was always rinsed with (double) distilled water.

5 Example I

Pyrex glass pretreated in the manner specified above was coated by means of spraying with Teflon of the type "Bakeware 955-2-63516". The Teflon coating had a thickness of 4-5 μm and after drying for 5 minutes at 105°C, was sintered at a temperature of 300°C for 15 minutes. The adhesion of the Teflon coating to the glass could be considered as especially good.

Example II

Pretreated Pyrex glass was coated by means of spraying with two layers of Teflon material, namely Teflon of the type "Electrical Appliances 459-520" in a thickness of 4-5 μm and Teflon of the type "Electrical Appliances 456-396", also in a thickness of 4-5 μm . Before the second Teflon layer was applied, the first Teflon layer was dried for 10 minutes at 105°C. After applying the second Teflon layer, the Teflon coating was sintered at a temperature of 400°C for 15 minutes.

The test plate obtained in accordance with this example had very good properties as regards the adhesion of the Teflon coating to the glass.

Example III

According to this Example, pretreated Pyrex glass was provided with two layers of Teflon. The primer layer of Teflon of the type "Industrial Fep 850-314" was applied by dipping, after which the top layer of "Industrial Fep 856-204" was applied by means of spraying.

The primer layer was dried for 10 minutes at a temperature of 105°C, the Teflon coating being sintered at a temperature of 315°C for 10 minutes after applying the top layer of Teflon.

The Teflon coating exhibited a very good adhesion to the glass surface.

Example IV

In accordance with the method described in Example III, pretreated Pyrex glass was provided with a Teflon primer of the type "Industrial Fep. 850-314" by means of dipping and, after a drying time of 10 minutes at 105°C with a top layer of Teflon of the type "Topcoat 456/395" by means of spraying. The Teflon coating was then sintered for 10 minutes at 430°C.

In the case of this test plate the adhesion of the Teflon coating to the glass surface is also especially good.

Example V

Symax glass pretreated in the manner specified above was coated with Teflon of the type "Bakeware 955-Z-63516" by means of spraying. The Teflon coating had a thickness of 4-5 µm and, after drying for 5 minutes at 105°C, was sintered at a temperature of 300°C for 15 minutes. The adhesion of the Teflon coating to the glass was assessed as especially good.

CLAIMS

1. Method for the application of a polytetrafluoroethylene (PTFE) coating to glass, characterized in that
 - a) the glass is subjected to a blasting treatment with an abrasive containing SiO_2 ;
 - b) the blasted surface of the glass is treated with an etchant;
 - c) the treated surface of the glass is exposed to the action of a grease-/oil-removing agent;
 - d) the glass with the oil-/grease-free surface is dried with an organic drying agent;
 - e) the glass is then freed from the drying agent in a dry, clean atmosphere; and
 - f) PTFE is applied to the treated surface of the glass.
2. Method according to Claim 1, characterized in that a material containing SiO_2 with a content of at least 95% SiO_2 is used as abrasive in step (a).
3. Method according to Claim 2, characterized in that quartz glass is used in step (a).
4. Method according to one or more of Claims 1-3, characterized in that an HF solution in water is used in step (b).
5. Method according to Claim 4, characterized in that a 5-15% HF solution in H_2O is used in step (b).
6. Method according to one or more of Claims 1-3, characterized in that a concentrated lye is used in step (b).
7. Method according to one or more of Claims 1-6, characterized in that a concentrated acid is used in step (c) as a grease-/oil-removing agent.
8. Method according to Claim 7, characterized in that HNO_3 or H_2SO_4 is used as concentrated acid.
9. Method according to one or more of Claims 1-8, characterized in that an alcohol such as methanol or ethanol is used in step (d) as organic drying agent.
10. Method according to one or more of Claims 1-8, characterized in that a ketone such as acetone is used

in step (d) as organic drying agent.

11. Method according to one or more of Claims 1-10, characterized in that step (e) is performed by means of purified compressed air.

12. Method according to one or more of Claims 1-11, characterized in that the PTFE is applied in step (f) in at most three layers.

13. Glass objects coated with PTFE obtained by use of the method according to one or more of Claims 1-12.

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/NL 87/00010**

I. CLASSIFICATION F SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC⁴: C 03 C 17/32		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC⁴	C 03 C 17/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	FR, A, 2103479 (VEB JENAER GLASWERK) 14 April 1972 see page 2, lines 9-35; claims 1-3 --	1-13
X	FR, A, 2033431 (AUTOLUBRIFICATION PRODUITS DE SYNTHESE APS) 4 December 1970 see claim 1; page 2, lines 1-15 --	1-13
A	GB, A, 1092473 (W.R. MIDWINTER LTD) 22 November 1967 -----	
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 6th August 1987	Date of Mailing of this International Search Report 27 AUG 1987	
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer L. ROSSI	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/NL 87/00010 (SA 17169)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 10/08/87

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 2103479	14/04/72	DE-A- 2124259	02/03/72
		CH-A- 562168	30/05/75
		SE-B- 369513	02/09/74
FR-A- 2033431	04/12/70	None	
GB-A- 1092473		None	

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82